



Research Paper

Role of oxygen vacancies in photocatalytic water oxidation on ceria oxide: Experiment and DFT studies

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ABSTRACT

Photocatalytic water oxidation suffers from sluggish kinetics and remains the bottleneck for water splitting. Here, using CeO₂ nanorods as model photocatalyst we studied the critical role of oxygen vacancies in photocatalytic water oxidation. First CeO₂ nanorods with similar morphology but different concentration of oxygen vacancies were fabricated by one-step hydrothermal method with in-situ reducing treatment. The optical absorption, charge transfer efficiency, and photocatalytic activity in oxygen generation were found closely dependent on the concentration of oxygen vacancies. Then density functional theory calculations were conducted to unveil the role of oxygen vacancies and understand the water oxidation mechanism. It was found the presence of oxygen vacancies narrows the bandgap and modulates the electronic structure for accelerating the charge transfer, in good agreement with the experimental observations. The overall oxygen generation pathway was screened and the oxygen vacancies were found to lower the barrier energy for the rate limiting step of O–O bond formation and restrain the reverse reaction of O and H, thus the O₂ generation kinetics on oxygen-defective CeO₂ are improved significantly. This study provides in-depth understanding on the critical role of oxygen vacancies in photocatalytic water oxidation and is helpful for designing highly efficient photocatalyst to overcome the bottleneck of water splitting.

1. Introduction

Photocatalytic water splitting is an effective way to harvest and utilize solar energy and produce hydrogen energy [1–5]. This process involves two reactions, namely hydrogen evolution and oxygen evolution. The first one has achieved much improvement in recent years [6], but oxygen evolution with a complex four electrons water oxidation remains a bottleneck to limit the efficiency due to the very slow kinetics [7–10]. Exploring a catalyst with high reactivity and capability of harvesting visible light is crucial and essential for photocatalytic water oxidation, though it remains a great challenge. Ceria (CeO₂) has been regarded as an attractive photocatalyst for oxygen evolution due to its strong redox capacity [11]. For example, Au/CeO₂ is reported to show high activity for visible-light-driven oxygen generation by means of surface-plasmon resonance effect [12], and CeO₂ nanorods with stepped (110) and (100) planes are much more active as compared with CeO₂ nanoparticles mainly exposed with (111) facets [13–16].

However, the wide band gap of CeO₂ (3.2 eV) depresses the ability

of harvesting visible light [11]. Oxygen vacancies (Vo) in metal oxides bring many benefits for photocatalysis like creating visible light absorption by generating isolated level below the conduction band and improving the donor density and electrical conductivity by providing shallow donors [17–22]. Actually, it has been reported that CeO₂ with oxygen vacancies exhibits good visible-light activity in photo-degradation of organic pollutants [23].

Furthermore, the detailed mechanism of water oxidation is complicated and not fully understood, especially the formation of O–O bond [24–26]. Therefore, unraveling the complex mechanism of water oxidation and the dependence of performance on structure are important for designing highly efficient photocatalyst. In this work, we choose CeO₂ as model to study the role of oxygen vacancies on photocatalytic water oxidation. Experimental study shows the oxygen-defective CeO₂ nanorods exhibit enhanced visible-light-harvesting, low electro-hole recombination and high oxygen evolution activity. Density functional theory (DFT) calculation confirms the presence of oxygen vacancies on CeO₂(110) effectively narrows the band gap, modulates

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the electronic structure to accelerate the charge transfer, and benefits the H₂O dehydrogenation and O₂ formation. So this work unveils the critical role of oxygen vacancies on photocatalytic oxygen generation, which is helpful for designing highly efficient photocatalyst to overcome the bottleneck of water splitting.

2. Experiments and methods

2.1. Synthesis of CeO₂ nanorods with and without oxygen vacancies

All the chemicals were purchased and used without further purification. CeO₂ nanorods with oxygen vacancies were synthesized by modifying previous method [27]. Briefly, in a 100 mL Teflon-lined autoclave Ce(NO₃)₃·6H₂O (1.736 g) and NaOH (19.2 g) were dissolved in distilled water (80 mL), afterward a certain amount (0.12, 0.24 and 0.48 g) of NaBH₄ was added and the solution was sealed and heated at 100 °C for 24 h. In this process, NaBH₄ serves as the reducing agent to in-situ generate oxygen vacancies during the growth of nanorods, and the concentration of oxygen vacancies can be controlled by the amount of NaBH₄ added. After cooling to room temperature, the precipitates were collected and then dispersed in a 1.0 M hydrochloric acid solution with stirring for 15 h at room temperature to remove NaBO₂ byproduct and residual NaBH₄. The resultant powders were collected through centrifugation, washing, and then drying at 60 °C overnight under vacuum. The final samples were labeled as CeO₂-NRs-1, CeO₂-NRs-2 and CeO₂-NRs-3, according to the amount of NaBH₄ added (0.12, 0.24 and 0.48 g), respectively. As reference, pristine CeO₂ nanorods (CeO₂-NRs) were prepared by hydrothermal method without NaBH₄.

2.2. Characterizations of catalysts

X-ray diffraction (XRD) patterns were recorded on D/MAX-2500 X-ray diffractometer equipped with Cu K α radiation with a scanning rate of 5°/min. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) observations were carried out on a Tecnai G2 F20 transmission electron microscope with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted with thermos ESCALAB 250XI system using Al K α radiation, and C 1 s peak (284.8 eV) of contamination carbon was applied to calibrate binding energy. Raman spectra patterns were measured by an inVia reflex DXR Microscope. Electron paramagnetic resonance (EPR) spectra were obtained by Bruker E500 spectrometer at 25 °C. Brunauer-Emmett-Teller specific surface area was calculated according to the nitrogen adsorption/desorption isotherms measured at −196 °C on a Micromeritics TriStar 3000 instrument. Photo-luminescence (PL) spectra were measured by a Horiba JobinYvon Fluorolog3-21 under the excitation light of 325 nm, and the UV–vis spectra were measured on Hitachi U-3010 spectrometer. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a sinusoidal ac perturbation of 10 mV applied over the frequency range of 0.01–10⁵ Hz.

2.3. Photocatalytic oxygen evolution

The photocatalytic oxygen generation reaction was conducted in a 120 mL closed reactor. 50 mg photocatalyst was dispersed in 100 mL distilled water with 0.17 g AgNO₃ as the electron sacrificial agent. After ultrasonic treatment 30 min, the reaction system was purged with argon gas to remove the dissolved air. Then, 300 W Xe lamp (PLS-SXE 300/300UV, Beijing Perfectlight Technology Co. Ltd.) with a UV cutoff filter ($\lambda > 420$ nm) vertically irradiated the reaction system from the upside position, the light density was 43 mW/cm² at 420 nm. The temperature was maintained at 0 °C, and the total reaction time was 4 h. The gas containing O₂ and Ar was withdrawn and analyzed by using Bruker 450-GC gas chromatograph equipped with a 5 A molecular sieve column and thermal conductivity detector, argon (99.999%) as

carrier gas.

2.4. Computational details

All DFT calculations were performed by using the Vienna ab initio simulation package (VASP) [28,29]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was applied to address the nonlocal exchange correlation energy [30]. To eliminate the error from strong self-interaction of localized Ce 4f-orbital, DFT + U method with the U_{eff} = 5.0 eV was used in all calculations [31,32]. The kinetic cutoff energy of 400 eV was adopted, and the Brillouin zone integration was sampled with the 3 × 3 × 1 k-point mesh. Structure optimization was deemed as converged until the force of all atoms less than 0.05 eV/Å, and the criteria of energy convergence was set to 1 × 10^{−5} eV. For the whole water oxidation reaction process, the climbing image nudged elastic band (CI-NEB) method was performed to locate the corresponding transition states (TS) [33].

Before model construction, CeO₂ bulk cell was optimized with a 6 × 6 × 6 k-point grid. The optimized lattice parameter is 5.473 Å, in agreement with the experimental value of 5.411 Å [34]. CeO₂(110) was used because the real CeO₂ nanorods exposed mainly with (110) facet according to the experiment results. As shown in Fig. 1a and b, a p (2 × 2) periodically repeated slab with five layers was constructed to represent the model of perfect CeO₂(110). During optimization, the bottom two layers were fixed in their bulk position, and others were fully relaxed. The vacuum region was set to 15 Å to avoid two slabs interaction. The model of CeO₂(110) is enough and suitable for our calculation after verification (Table S1). Similar to the previous calculation [35,36] and our experiment results (see below), one sub-surface oxygen atom from the perfect CeO₂(110) was removed to simulate the oxygen defective CeO₂(110) with a formation energy of 268.1 kJ/mol (Fig. 1c and d). The adsorption energy (E_{ads}) is defined as follows.

$$E_{\text{ads}} = E_{\text{adsorbate/substrate}} - E_{\text{adsorbate}} - E_{\text{substrate}}$$

where $E_{\text{adsorbate/surface}}$, $E_{\text{adsorbate}}$ and $E_{\text{substrate}}$ represent the energies of substrate with the adsorbate species, the adsorbate molecule, and the substrate, respectively. A negative value means the process is exothermic adsorption.

3. Results and discussion

3.1. Structure characteristic of catalysts

Oxygen-defective CeO₂ nanorods were synthesized via one-step hydrothermal method with in-situ reducing treatment. Fig. 2a shows the typical XRD pattern of as-prepared CeO₂ nanorods, from which eight main diffraction peaks at $2\theta = 28.54^\circ$, 33.04° , 47.43° , 56.31° , 59.08° , 69.33° , 76.68° and 79.05° belonging to the (111), (200), (220), (311), (222), (400), (331) and (420) plane of cubic fluorite ceria (JCPDS card: 34-0394) are observed. There is no phase change in oxygen-defective CeO₂ compared with the pristine one, and no peak of any other impurity is detected. TEM images in Fig. 2b–e show that CeO₂ exhibits nanorods morphology with the length of pristine CeO₂-NRs as about 95 nm and the diameter as about 9.0 nm. The adding of reductant in the synthesis makes the rods slightly shorter and bigger, but does not change the overall morphology. HRTEM image and electron diffraction in Fig. 2f further reveals the nanorods are polycrystalline faceted with mainly (110). The specific surface area changes slightly in range of 98–112 m²g^{−1} (Table 1).

To reveal oxygen vacancies of CeO₂ nanorods, EPR, XPS and Raman characterizations were conducted. As shown in Fig. 3a, similar to other metal oxides, CeO₂ shows a symmetrical EPR signal ($g = 2.003$) originated from the unpaired electrons at oxygen vacancy sites [18,21,37]. Notably, CeO₂-NRs-2 shows the strongest signal, followed by CeO₂-NRs-1, CeO₂-NRs-3 and finally CeO₂-NRs, indicating the order of Vo concentration in the samples. In particular, the very intensive signal of

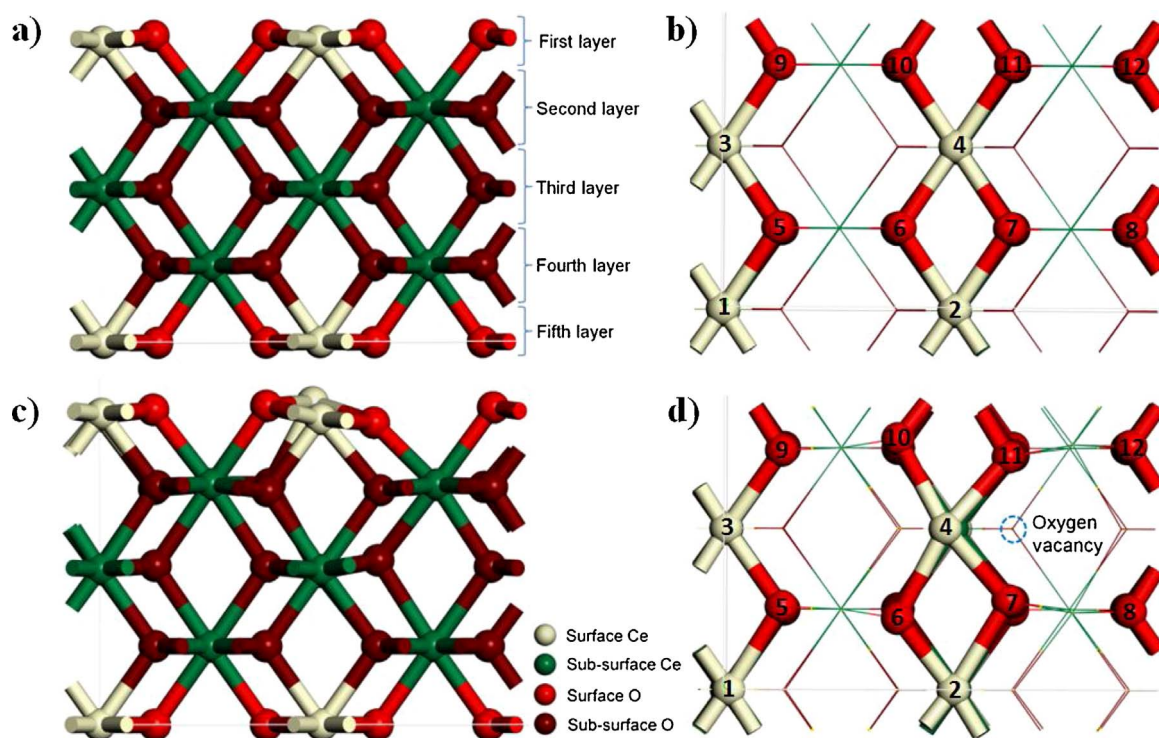


Fig. 1. Optimized surface configuration of CeO₂(110): (a) and (b) are side and top views of perfect CeO₂(110), (c) and (d) are side and top views of oxygen-defective CeO₂(110).

CeO₂-NRs-2 suggests it is more abundant with Vo compared with CeO₂-NRs-1, attributed to the more NaBH₄ in the synthesis mixture. However the Vo becomes less in CeO₂-NRs-3 when more NaBH₄ are added, probably because large amount of NaBO₂ are formed on CeO₂ surface that suppresses the further reduction reaction. In Ce-3d XPS spectra shown in Fig. 3b, the Ce 3d peak of CeO₂-NRs-1, 2, and 3 shifts to lower binding energy compared with CeO₂-NRs, confirming the formation of oxygen defects on the surface. The peak is further fitted into eight peaks to distinguish Ce³⁺ and Ce⁴⁺ species [14,23,27], and Table 1 shows the weight of Ce³⁺ based on the integrated area of these peaks increases firstly from CeO₂-NRs to CeO₂-NRs-1 and CeO₂-NRs-2 and then decreases for CeO₂-NRs-3, agreeing well with the tendency obtained from EPR measurement in Fig. 3a. Raman spectra in Fig. 3c shows strong signal at ~450 and weak peak at ~600 cm⁻¹ originated from the fluorite type structure vibration [27,38] and the presence of Ce³⁺ correlated to oxygen vacancies [27,39], respectively. And the reduced samples show almost four times higher ratio of the two peaks area (A₆₀₀/A₄₅₀) compared with the pristine counterpart as summarized in Table 1, also confirming the existence of large amount of oxygen vacancies. It is worth noting that, EPR and Raman characterizations show significant difference between the reduced and pristine CeO₂, but the difference derived from XPS analysis is relatively small. This suggests that the oxygen vacancies are richer in the inner lattice of CeO₂, note XPS can only test the surface layers but EPR and Raman reflect the average structure of the bulk.

3.2. Photocatalytic performance of catalysts

To evaluate the optical properties of CeO₂ nanorods, UV–vis diffuse reflectance spectroscopy (DRS) was measured, and Fig. 4a shows that the oxygen-defective CeO₂ samples exhibit extended visible-light adsorption. Specially, the band gap of CeO₂-NRs-2 decreased by 0.23 eV compared to CeO₂-NRs (2.76 eV), also the band gap of CeO₂-NRs-1 and CeO₂-NRs-3 are reduced to 2.65 and 2.71 eV respectively. The increased visible light adsorption can be originated from the electron transition from the valence band to oxygen defect level or from the defect level to conduction band [18]. Additionally, the PL spectra in

Fig. 4b demonstrate the oxygen-defective CeO₂ nanorods have lower PL intensity compared to the pristine sample, and the order of separation efficiency is CeO₂-NRs-2 > CeO₂-NRs-1 > CeO₂-NRs-3 > CeO₂-NRs, indicating good dependence on the Vo concentration. The electrochemical impedance spectroscopy (EIS) in Fig. 4c shows that CeO₂-NRs-2 has a much smaller arc radius compared to pristine CeO₂-NRs, suggesting the very low resistance and fast interfacial charge carrier transfer [40–43].

The photocatalytic oxygen generation was tested under visible light (Fig. 4d). Obviously, CeO₂-NRs-2 shows the highest photocatalytic activity with the highest oxygen evolution rate (137.7 μmol g⁻¹ h⁻¹), followed by the CeO₂-NRs-1 (101.9 μmol g⁻¹ h⁻¹), CeO₂-NRs-3 (83.5 μmol g⁻¹ h⁻¹) and CeO₂-NRs (78.9 μmol g⁻¹ h⁻¹). To eliminate the effect of surface area, the reaction rate was normalized by the surface area. However, these catalysts still show the same tendency of CeO₂-NRs-2 (1.224 μmol m⁻² h⁻¹) > CeO₂-NRs-1 (0.994 μmol m⁻² h⁻¹) > CeO₂-NRs-3 (0.887 μmol m⁻² h⁻¹) > CeO₂-NRs (0.804 μmol m⁻² h⁻¹). So it is concluded that the oxygen evolution activity is closely dependent on the concentration of oxygen vacancy in CeO₂, namely the more concentration of Vo in CeO₂, the higher the oxygen evolution activity.

3.3. Influence of oxygen vacancies on electronic structure of CeO₂

In order to get insights on the role of oxygen vacancies, and to understand the reaction mechanism of oxygen evolution, DFT + U calculations were conducted. It is well known that the photo-induced electron/hole strongly depends on the band structure and electronic density of states (DOS) of photocatalyst [44]. As shown in Fig. 5a and b, the valence band (VB) of CeO₂(110) is mainly contributed by the O-2p orbit below Fermi level and the conduction band (CB) is ascribed to the Ce-4f orbit above Fermi level. However, the bandgap (E_g) is underestimated by using DFT calculation due to the derivative discontinuity of exchange correlation function [45,46]. The presence of oxygen vacancies effectively reduces the bandgap, which is consistent with the enhanced optical absorption in Fig. 4a. The VB width of oxygen-defective CeO₂(110) increases compared to that of perfect CeO₂(110), predicting a higher holes mobility and a better photocatalytic oxidation

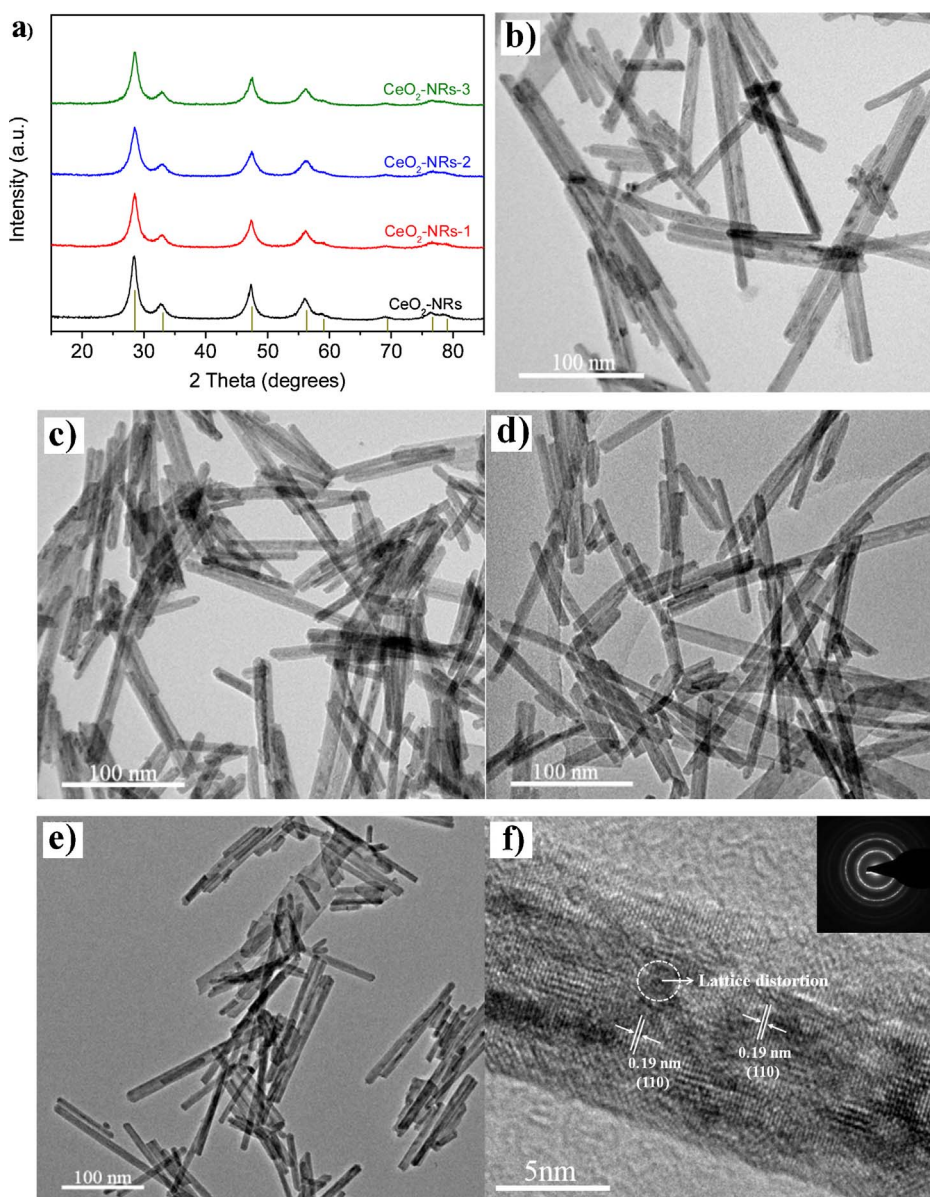


Fig. 2. (a) XRD patterns, TEM images of (b) CeO₂-NRs, (c) CeO₂-NRs-1, (d) CeO₂-NRs-2, (e) CeO₂-NRs-3 and (f) HRTEM image of CeO₂-NRs-2 (inset: Fast-Fourier transform pattern image).

ability of holes [43,47]. Meanwhile, the presence of Vo reduces the effective mass of electron because of the relative stronger no-localization of Ce-4f state (Fig. 5b). The smaller the electron effective mass, the higher the mobility of electrons [48]. Therefore, the separation of photo-induced electrons and holes will be enhanced in the oxygen-defective CeO₂. The Bader charge analysis [49,50] and charge density difference [51,52] (Fig. S2) were also carried out to clarify the effect of oxygen vacancies. As shown in Table S2, the average net charges of surface O atoms on perfect and oxygen-defective CeO₂(110) are −1.143 and −1.178 lel, and the average net charges of surface Ce are

+2.302 and +2.246 lel, respectively. Obviously, more electrons enrich on the surface of oxygen-defective CeO₂(110) owing to the presence of oxygen vacancies, and therefore an internal electric field is created. As such, the photoexcited electron-hole pairs will be effectively separated, as confirmed by the experimental measurements.

3.4. Role of oxygen vacancies on water oxidation

3.4.1. Dehydrogenation of H₂O

Firstly, the sequential dehydrogenation of water was considered in

Table 1

Structure characteristics of pristine and oxygen-defective CeO₂ (^a obtained from Raman spectra, ^b calculated from XPS analysis).

Samples	Specific surface area/m ² g ^{−1}	Length (nm)	Diameter (nm)	Pore size	Pore volume	^a A ₆₀₀ /A ₄₅₀	^b Surface Ce ³⁺ /%
CeO ₂ -NRs	98.1	95 ± 5	9.0 ± 0.5	16.5	0.180	0.061	12.20
CeO ₂ -NRs-1	102.5	80 ± 5	9.0 ± 0.5	17.9	0.266	0.202	16.84
CeO ₂ -NRs-2	112.5	75 ± 5	10.0 ± 0.5	14.6	0.239	0.260	18.75
CeO ₂ -NRs-3	94.1	95 ± 5	10.0 ± 0.5	19.7	0.244	0.254	17.67

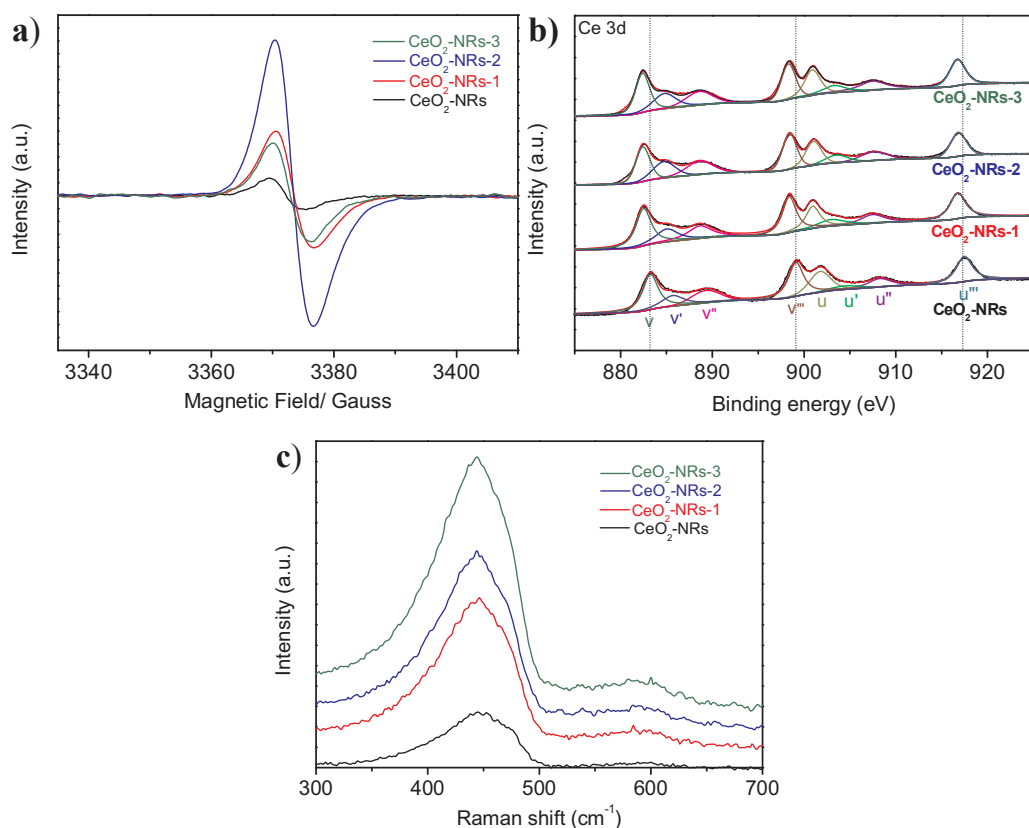


Fig. 3. (a) Room temperature EPR spectra, (b) Ce-3d XPS spectra, and (c) Raman spectra of pristine and oxygen-defective CeO₂.

the computation, namely $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \rightarrow \text{O} + 2\text{H}$, as shown in Fig. 6. On perfect CeO₂(110), H₂O is adsorbed on the top Ce site with an adsorption energy of -76.19 kJ/mol, close to reported data [53]. The adsorbed H₂O dehydrogenate to OH and H, and in the final state (FS) OH still binds to the Ce site but H migrates to neighboring top O site.

This step is exothermic by -28.93 kJ/mol with the activation energy of 7.72 kJ/mol. Subsequently, the formed OH group dissociates to O and H via the O–H bond scission. This elementary step needs to overcome high activation energy of 77.15 kJ/mol with endothermicity of 67.51 kJ/mol.

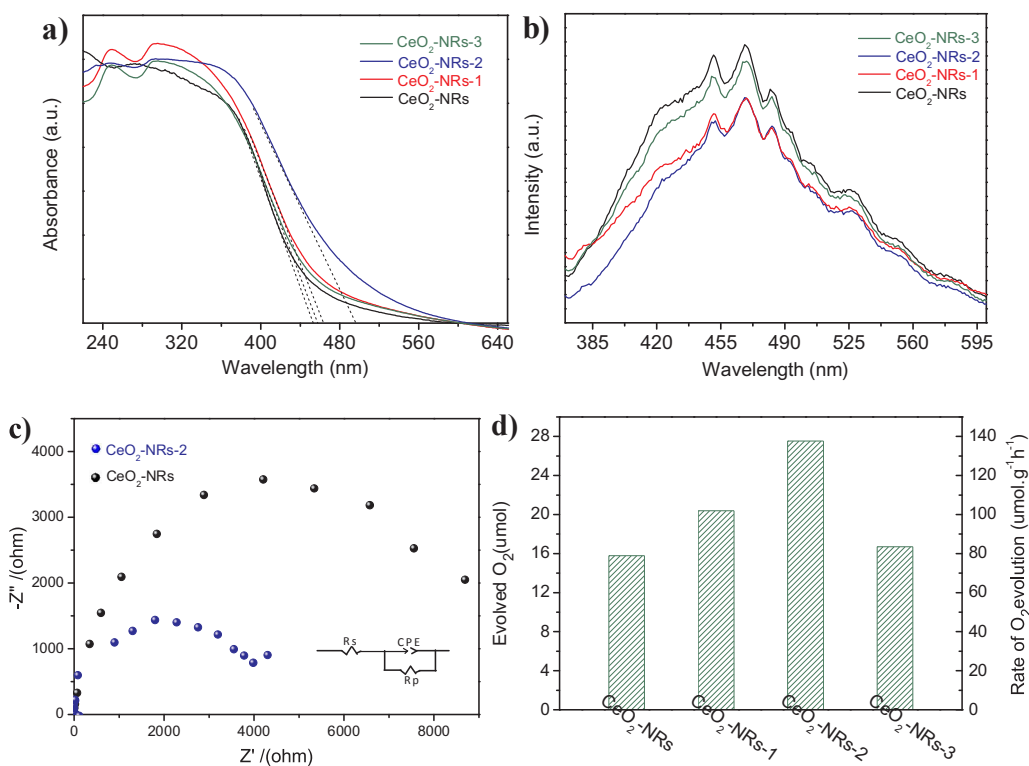


Fig. 4. (a) UV-vis DRS spectra, (b) PL spectra, (c) Electrochemical impedance spectroscopy (EIS), and (d) Visible-light photocatalytic oxygen evolution of pristine and oxygen-defective CeO₂.

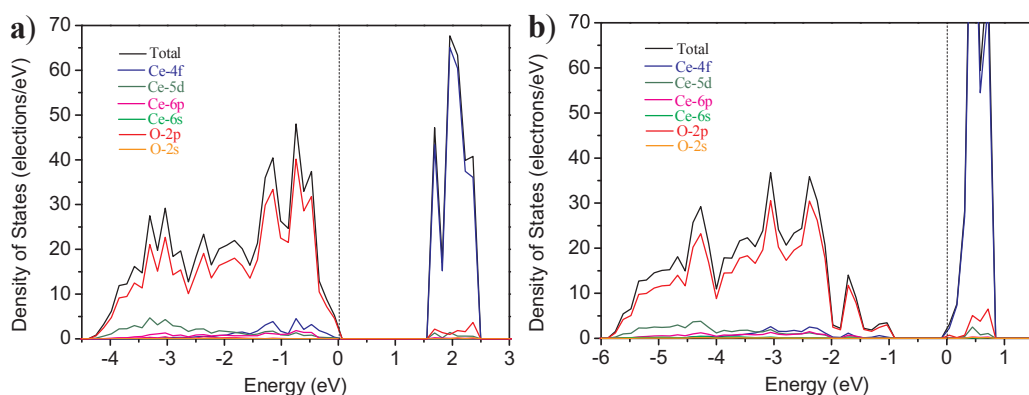


Fig. 5. Total density of states (DOS) and projected density of states (PDOS) of (a) perfect CeO₂(110) and (b) oxygen-defective CeO₂(110). The dotted lines at energy zero represent the Fermi level.

The reaction on oxygen-defective CeO₂(110) is similar to the case on perfect CeO₂(110), but easier. H₂O is bounded on Ce site a little weakly (−67.51 kJ/mol), and undergoes a spontaneous O–H cracking without any activation energy to produce OH and H, with exothermic by −71.37 kJ/mol. Then the OH group further dissociates to H and O with much lower activation energy of 48.22 kJ/mol and endothermicity of 9.64 kJ/mol, respectively.

It is clear that the dissociation of H₂O to OH and H on CeO₂(110) is easy to occur and even barrierless. However, regarding to the further dissociation of OH, there is a fatal problem for perfect CeO₂(110), namely the formed O and H tend to combine with each other to produce OH again, because the reverse O + H → OH reaction is more facile than the forward OH → O + H reaction (activation energy 9.64 vs 77.15 kJ/mol). On the oxygen-defective CeO₂(110), fortunately, the OH dehydrogenation is enhanced due to the decreased activation energy (48.22 kJ/mol), but the reverse recombination reaction is effectively restrained due to the increased binding strength of O + H as a result of more electrons transfer from O to the neighboring Ce (Table S3). Therefore, the presence of oxygen vacancies plays a crucial role in improving the production of O intermediates.

3.4.2. Formation of O₂

Regarding to the O–O bond coupling, two possible ways were considered. For the first one, the second H₂O was dehydrogenated to H and OH, and then the OH combines with the O from the first H₂O molecule to form OOH, namely, O + 2H + H₂O → OOH + 3H. For another one, the second H₂O directly reacts with OH and H of the first H₂O to form HOOH, namely OH + H + H₂O → HOOH + 2H. The corresponding details are presented in the supporting information of Fig. S3, and due to the high activation energy, the HOOH pathway is un-possible on both perfect and oxygen-defective CeO₂(110). Therefore, the first pathway of OOH formation with lower activation energy is considered in the follows.

On the perfect CeO₂(110) (Fig. 7, TS4), the O on top Ce site formed

by first H₂O interacts with the OH formed from the dehydrogenation of the second H₂O towards formation of O–O bond in form OOH. This is also verified by the projected density of states (PDOS) analysis (Fig. 8) that shows large overlaps between O-s, p states of O atom from the first H₂O and the s, p states of OH from the second H₂O, suggesting an orbital hybridization occurs for O–O bonding. The formed OOH species bind to Ce site in the FS, which needs to overcome relative high activation energy of 83.90 kJ/mol with endothermicity of 0.96 kJ/mol. Then the OOH dehydrogenate to O₂ and H via the O–H bond scission with the activation energy and reaction energy of 18.32 and −27.00 kJ/mol, respectively.

On the Oxygen-defective CeO₂(110) (Fig. 7, TS6), the distance between O and OH is 2.394 Å, shorter than that on the perfect CeO₂(110) (2.912 Å), indicating the interaction between O and OH is much stronger on the oxygen-defective surface. This step has a much lower activation energy of 65.58 kJ/mol compared with the case of perfect CeO₂(110). Overall the O–O bond formation represents the rate-limiting step in the whole water oxidation, and the presence of oxygen vacancies on CeO₂(110) significantly reduces the activation energy of this step, due to the decreased O binding strength with relative less electrons transferred between O and Ce (see Table S4).

The rate constant of key elementary steps involved in water oxidation were calculated according to the harmonic transition theory [54,55]. As shown in Table S5, it is clear that oxygen-defective CeO₂(110) has higher rate constant of key elementary steps than that on perfect CeO₂(110). Specially, the rate constant of rate-limiting step on oxygen-defective CeO₂(110) is about 2–3 orders of magnitude higher than that on perfect CeO₂(110), confirming the critical roles of oxygen vacancy in water oxidation from the perspective of kinetic.

4. Conclusions

We unveiled the important role of oxygen vacancies in photocatalytic water oxidation using CeO₂ nanorods as model catalyst by

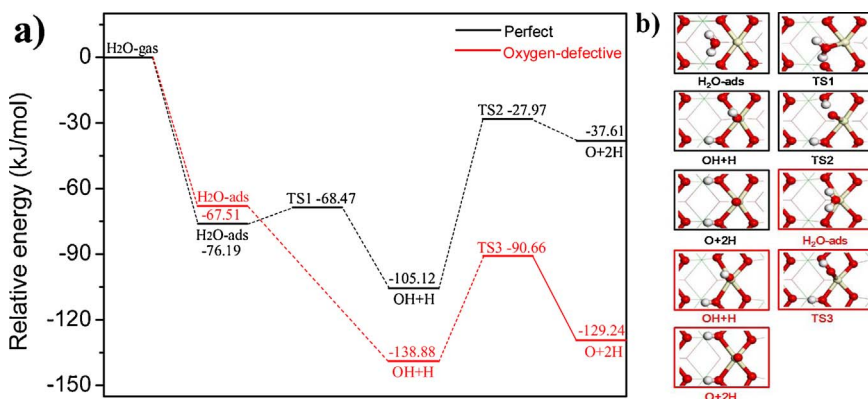


Fig. 6. (a) Potential energy profiles for water dehydrogenation to O, and (b) the corresponding optimized geometries for related states on perfect and oxygen-defective CeO₂(110) surfaces.

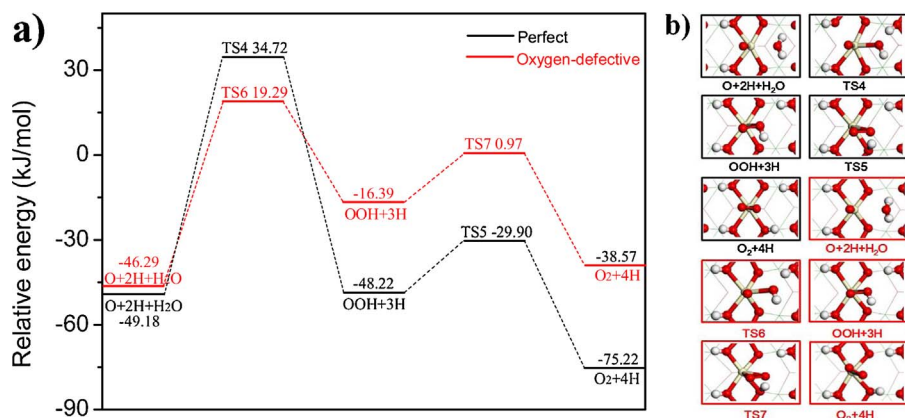


Fig. 7. (a) Potential energy profiles for O–O bond formation, and (b) the corresponding optimized geometries for related states on perfect and oxygen-defective $\text{CeO}_2(110)$ surfaces.

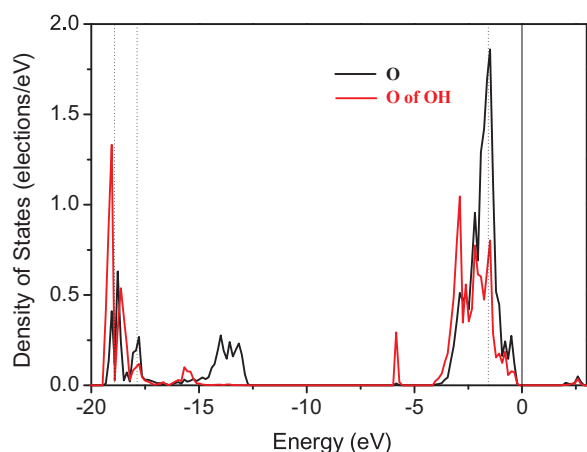


Fig. 8. DOS of O (from the first H_2O) and O (from the second H_2O) on perfect $\text{CeO}_2(110)$. The solid line at energy zero represents Fermi level, and the dotted lines shows the overlaps between the O and OH.

experimental and DFT studies. CeO_2 nanorods synthesized with in-situ reduction during the hydrothermal growth are abundant with oxygen vacancies from the bulk to surface, with the optical absorption, charge separation and transfer being improved with the increase of oxygen vacancies. The photocatalytic activity also shows good correlation with the concentration of oxygen vacancies. Furthermore, DFT + U calculation shows the presence of oxygen vacancies on $\text{CeO}_2(110)$ effectively narrows the band gap and accelerates the charge separation by regulating the electronic structure. More importantly, on oxygen-defective $\text{CeO}_2(110)$ the barrier energy for the rate limiting step of O–O bond formation in the whole water oxidation is decreased, along with restraining the reverse reaction of O and H, thus the O_2 generation kinetics are improved significantly.

Competing interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.10.049>.

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